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Asymptotic Behavior of the Ground State of Large Atoms

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Abstract

We review some results on the behavior of the ground state energy and the ground state density for large atoms as the nuclear charge Z increases to infinity. Here the atom is described by various models, namely the Thomas-Fermi, the Thomas-Fermi-Weizsäcker, the Fermi-Hellmann, the Hellmann-Weizsäcker model, and the Schrödinger equation.

1 Introduction

The following results for large atoms, i.e., for large nuclear charge Z and large electron number N keeping the ratio Z/N = \( \alpha \) fixed, shall be presented:

- Asymptotic behavior of the ground state energy,
- Bounds on the excess charge,
- Asymptotic behavior of the ground state density.

The results will be presented in the context of the following models ordered roughly according to increasing complexity:

1. The Thomas-Fermi model (Thomas [20], Fermi [7, 6]):

\[
\mathcal{E}_{TF}(\rho) = \int \frac{3}{5} \left( \frac{6\pi^2}{q} \right)^{2/3} \rho(r)^{5/3} - \frac{Z}{|r|} \rho(r) + \frac{1}{2} (\rho \ast \frac{1}{| \cdot |})(r) \rho(r) \, d^3r
\]  \hspace{1cm} (1)

\[
\rho \geq 0, \quad \int \rho \leq N,
\]  \hspace{1cm} (2)

\( q \) being the number of spin states of one electron, i.e., \( q=2 \).
2. The Thomas-Fermi-Weizsäcker model (von Weizsäcker [21]):

\[ E_{TFW}(\rho) = \int (\nabla \sqrt{\rho(r)})^2 + E_T(\rho) \]  

with the conditions (2).

3. The Fermi-Hellmann model (Fermi [7], Hellmann [8]):

\[ E_H(\rho) = \sum_{l=0}^{\infty} \int_0^\infty \left( \frac{3}{2(q+\frac{1}{2})} \rho_l(r)^3 + \left( \frac{(l+\frac{1}{2})^2}{r^2} - \frac{Z}{r} \right) \rho_l(r) dr \right) \]

\[ + \frac{1}{2} \sum_{l,l'=0}^{\infty} \int_0^\infty \int_0^\infty \rho_l(r) \rho_{l'}(r') \max\{r,r'\} dr dr', \]  

\[ \rho_l \geq 0, \sum_{l=0}^{\infty} \int_0^\infty \rho_l(r) dr \leq N. \]  

4. The Hellmann-Weizsäcker model (Hellmann [8])

\[ E_{HW}(\rho) = \sum_{l=0}^{\infty} \int_0^\infty \rho_l(r) dr + E_H(\rho) \]  

with condition (5).

5. The Schrödinger model

\[ E_Q(Z,N) = \inf\{ (\psi,H\psi) | \psi \in Q(H), ||\psi|| = 1 \} \]  

where

\[ H = \sum_{i=1}^{N} \left( -\Delta_i - \frac{Z}{|r_i|} \right) + \sum_{1 \leq j < i}^{N} \frac{1}{|r_i - r_j|} \]

as self-adjoint realization on \( \bigwedge_{i=1}^{N} (L^2(\mathbb{R}^3) \otimes C^q) \).

We remark that basic properties of the first four models – such as existence of minimizers in suitable functions spaces – are well known (Lieb [12] and Siedentop and Weikard [15]). – We shall mention some more results for the models 1, 2, 4, and 5 but shall concentrate mainly on the Fermi-Hellmann equations.

2 Asymptotic Behavior of the Ground State Energy

Denote the infima of the functionals by roman \( E \) – the functionals are denoted by caligraphic \( E \). With this notation we can formulate the following results:
1. 

\[ E_{TF}(Z, N) = E_{TF}(1, \alpha)Z^{7/3} \]  

(9)

where \( \alpha = Z/N \). This is immediate by scaling, i.e., choosing \( \rho(r) = Z^2 \rho_1(Z^{1/3}r) \) in (1) (Fermi [6]). In particular, the Thomas-Fermi energy behaves exactly proportional to \( Z^{7/3} \), if \( \alpha \) is fixed.

2. 

\[ E_{TFW}(Z, N) = E_{TF}(Z, N) + D Z^2 + o(Z^2) \]  

(10)

for fixed \( D = \frac{2}{3\pi^2} I_1 \) and \( I_1 = \int (\nabla \psi)^2 \approx 8.583897 \), \( \psi \) being the positive solution of

\[ \left(-\Delta + \left(\frac{6\pi^2}{q}\right)^{2/3} \left|\psi\right|^{4/3} - Z|\psi|^{-1}\right)\psi = 0 \]  

(11)

(Lieb [12]).

3. 

\[ E_H(Z, Z) = E_{TF}(Z, Z) + O(Z^{5/3}) \]  

(12)

(Siedentop and Weikard [17], Weikard [22]).

We indicate the proof of (12). To this end we observe some facts for the Fermi-Hellmann model: The minimizer of \( E_H \) fulfills the Euler-Lagrange equation

\[ \rho_l(r) = \frac{2q(l + \frac{1}{2})}{\pi} \left[ (\varphi(r) - \frac{(l + \frac{1}{2})^2}{r^2})^{1/2} \right]_{+}^{l} \quad l = 0, 1, 2, ... \]  

(13)

\[ \varphi(r) = \frac{Z}{r} - \sum_{l=0}^{\infty} \int_{0}^{\infty} \frac{\rho_l(r')}{{\max}\{r, r'\}} dr'. \]  

(14)

Moreover by Legendre transform the dual variational principle of the Hellmann principle is

\[ \mathcal{F}_H(Z, \mu)(\psi) = -\frac{1}{2} \int_0^\infty (r\psi)'^2 dr - \frac{2}{3} \sum_{l=0}^{\infty} 2q(l + \frac{1}{2}) \int_0^\infty \left[ \psi(r) - \frac{(l + \frac{1}{2})^2}{r^2} + \mu \right]^{3/2} dr \]  

(15)

with \( (r\psi)' \in L^2(IR^+) \), \( r\psi(r) \to Z \) for \( Z \to 0 \), and \( \psi(r) = O(1/r) \) as \( r \to \infty \).

For the supremum \( F_H(Z, \mu) \) of this functional we have

\[ F_H(Z, \mu) + \mu N = E_H(Z, N); \]  

(16)

\[ N = \sum_{l=0}^{\infty} \frac{2q(l + \frac{1}{2})}{\pi} \int_0^\infty \left[ \psi_{max}(r) - \frac{(l + \frac{1}{2})^2}{r^2} + \mu \right]^{1/2} dr, \]

where \( \psi_{max} \) is the maximizer of (15).
For the proof of (12) one chooses

$$\psi(r) = \varphi_{TF}(r) = \frac{Z}{r} - \int_0^\infty \frac{\rho_{TF}(r')}{|r - r'|} d^3 r'$$

(17)

for the lower bound, where $\rho_{TF}$ is the minimizer of $E_{TF}$, in the lower bound and $\rho_l$ as in (13) substituting $\varphi$, however, by $\varphi_{TF}$. The result follows then from the fact that the minimizer of $E_H$ has always particle number $\int_0^\infty \sum_{i=0}^\infty \rho_i(r) dr$ smaller than $Z$ (see Section 3), i.e., we use allowed trial functions, and the explicit summation over the angular momenta $l$. This may be done by Poisson summation or more directly by using a convexity argument (see equation (39) for a similar result).

\begin{enumerate}
\item $E_{HW}(Z, Z) = E_{TF}(Z, Z) + O(Z^2)$
\end{enumerate}

(Siedentop and Weikard [18, 17, 16]).

\begin{enumerate}
\item $E_Q(Z, N) = E_{TF}(Z, N) + \frac{9}{8} Z^2 + O(Z^{47/24})$
\end{enumerate}

(19)

where $Z/N = \alpha$ is fixed.

This has been conjectured by Scott [14]. The first term was established by Lieb and Simon [13]. The proof of (19) has been given by Siedentop and Weikard [17, 16] (see also Hughes [9] for the lower bound) for the neutral case and has been extended to general $\alpha$ by Bach [1].

We wish to outline the proof for $Z = N$. A lower bound may be obtained by an estimate on the indirect part of the Coulomb energy (Lieb [11]). It turns out that

$$E_Q(Z, Z) \geq Z^{4/3} \inf \sigma \left( \sum_{i=1}^N h_{TF,i} \right) - \frac{1}{2} \int \rho_{TF} \varphi \rho_{TF} \varphi^{-1} d^3 r + O(Z^{5/3})$$

(20)

$$h_{TF,i} = \underbrace{1 \otimes \ldots \otimes 1}_{i-1 \text{ factors}} h_{TF} \otimes \underbrace{1 \otimes \ldots \otimes 1}_{N-i \text{ factors}}$$

$$h_{TF} = -Z^{-2/3} \Delta + \varphi_{TF,1}$$

(21)

where $\varphi_{TF,1}$ is the Thomas-Fermi potential (17), however for $Z = 1$. Thus the first summand on the right hand side of (20) may be estimated from below by $Z^{4/3}$ times the sum of all negative eigenvalues of $h_{TF}$. We observe that (21) can be broken up into a set of uncoupled ordinary differential equations (decomposition into angular momentum channels). A careful WKB analysis for high angular momenta and summing up the "bare" Coulomb eigenvalues for low angular momenta yields the answer up to errors of order $Z^{17/9} \log Z$. 

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The upper bound may be obtained by choosing an appropriate “trial” operator $d_1$

$$0 \leq d_1 \leq 1, \quad d_1 \in \mathcal{L}(L^2(\mathbb{R}^3) \otimes C^\infty), \quad \text{tr} \, d_1 \leq N,$$  \hspace{1cm} (22)  

a so called one-particle density matrix in the inequality

$$E_Q(Z, N) \leq \text{tr}[-(\Delta - Z/|.| + \frac{1}{2}V)d_1]$$  \hspace{1cm} (23)  

where $V = \rho |.|^{-1}$, $\rho$ being the density of $d_1$, i.e., formally $\rho(r) = \sum_{\sigma=1}^q d_1(r, \sigma, r, \sigma)$. After some intermediate steps one obtains

$$E_Q(Z, Z) \leq \mathcal{E}_H(\rho) + \frac{q}{8}Z^2 + O(Z^{47/24}).$$  \hspace{1cm} (24)  

Equation (12) completes the proof.

3 Bounds on the Excess Charge

Let $E$ denote any of the above energies

$$N_c = \inf\{|N|E(Z, N) = E(Z, N + k) \text{ for all } k \in \mathbb{N}\}$$  \hspace{1cm} (25)  

The maximal excess charge is then $Q_c = N_c - Z$. It may be easily shown that $Q_c$ is nonnegative in all of the above models. In the following we wish to discuss some upper bounds on $Q_c$.

- The Thomas-Fermi and Fermi-Hellmann model:

$$Q_c^{TF} = Q_c^H = 0$$

(Lieb and Simon [13], Siedentop and Weikard [15]). Here we indicate the proof of this result for the Fermi-Hellmann case. Let $\rho_1, \rho_2, \ldots$ be the absolute minimizer of the Fermi-Hellmann functional. Assume $N_c < Z$. Then

$$Z > N_c = \int_0^\infty \sum_{l=0}^\infty \rho_l \, dr = \sum_{l=0}^\infty \frac{q2(l+1/2)}{\pi} \int_0^\infty \left[\varphi(r) - \frac{(l+1/2)^2}{r^2}\right]_+^1 \, dr$$

$$\geq \frac{q}{\pi} \int_0^\infty \left[\frac{Z-N_c}{r} - \frac{1}{4r^2}\right]_+^1 \, dr = \infty$$  \hspace{1cm} (26)  

which is a contradiction. On the other hand assume $N_c > Z$. Then there is an $R$ such that $\varphi(r) < 0$ for $r > R$. Then $(r\varphi)'' = 0$ in this region, i.e., $\varphi(r) = a + \frac{b}{r}$. Since $\varphi(\infty) = 0$ the constant $a$ is zero and $b$ negative. Because of the continuity of $\varphi$, $\varphi(r) < 0$ on $\mathbb{R}^+$ which cannot hold. The Thomas-Fermi case can be treated analogously.
• For the Thomas-Fermi-Weizsäcker model one has

\[ Q_{TFW}^e \leq 178.03 \frac{q}{6\pi^2} \quad (27) \]

(Benguria and Lieb [3], Solovej [19]) This bound is obtained by an universal (Z independent) bound on the potential and a bound on the density in terms of the potential.

• In the quantum mechanical case the following bounds are known

\[ Q_{el}^4 \leq Z \quad (28) \]

(Lieb [10]) and

\[ Q_{el}^4 = O(Z^{47/56}) \quad (29) \]

(Fefferman and Seco [5, 4]). The proof of (29) uses (19) together with the fact that the nucleus is screened out already at small distances.

4 Asymptotic Behavior of the Ground State Density

Let \( d = \frac{18\pi}{q} \). Then:

• Thomas-Fermi model:

\[ \varphi_{TF}^Z(r) \leq \min\left\{ \frac{d^2}{r^4}, \frac{Z}{r} \right\} \quad (30) \]

for \( Z, r > 0 \), where \( \varphi_{TF}^Z \) is the Thomas-Fermi potential for charge \( Z \). Moreover, \( \varphi_{TF}^Z \) is monotone in \( Z \) and the limiting function is

\[ \varphi_{TF}^{\infty}(r) = \frac{d^2}{r^4} \]

This follows immediately from comparison arguments.

• Thomas-Fermi-Weizsäcker model:

In this subsection we use units such that the constant in front of the \( \rho^{5/3} \) term in (3) is 3/5.

\[ \varphi_{TFW}^Z(r) \leq \chi(\alpha)r^{-4} + \frac{\pi^2}{\alpha^2}r^{-2} \quad (32) \]

where \( \chi \) is given as

\[ \chi(\alpha) = \begin{cases} 9\pi^{-2} + c\alpha^{-4} & 0 \leq \alpha \leq \alpha_0 \\ 25\pi^{-2s}(1 - \alpha)^{-4} & \alpha_0 < \alpha < 1 \end{cases} \]
and \((C, \alpha_0)\) is chosen such that \(\chi \in C^1([0,1])\) and \(\tau = \frac{1}{2} + \frac{\sqrt{3}}{2}\). (Benguria and Lieb [3], Solovej [19])

\[
\varphi_{TFW}^Z(r) \to \varphi_{TFW}^\infty(r)
\]  

(33)

and

\[
\varphi_{TFW}^\infty(r) = 9\pi^2 r^{-4} - \frac{27}{4} \pi^{-2} - \frac{25}{64} \pi^4 r^2 - \frac{37}{768} \pi^4 r^2 + O(r^{-\frac{1}{2} + \frac{\sqrt{3}}{2}}).
\]  

(34)

Solovej obtains also the corresponding limit for the density.

- **Fermi-Hellmann model:**
  The following results are from Bach and Siedentop [2].

\[
\varphi_H^Z(r) \leq \min \left\{ \frac{Z}{r}, \left( \frac{d}{r^2} + \frac{1}{2r} \right)^2 \right\}
\]  

(35)

There exists some \(R\) such that for \(r > R\) we have

\[
\varphi_H^Z(r) \geq \frac{1}{4r^2}.
\]  

(36)

\(\varphi_H^Z(r)\) is monotone increasing in \(Z\)

\[
\varphi_H^\infty(r) = \frac{d^2}{r^4} + O(r^{-5/2}) \quad \text{at 0},
\]  

(37)

and

\[
\varphi_H^\infty(r) = \frac{1}{4r^2} + o(r^{-2}) \quad \text{at } \infty.
\]  

(38)

The first inequality in (35) is immediate by writing \(\varphi_H^Z\) in terms of \(\rho_i\). To prove the second inequality we use the following lemma

\[
-\frac{1}{3} \left( \eta - \frac{1}{4} \right)^{3/2} \leq \sum_{l=0}^{\infty} \eta(l + \frac{1}{2}) \left[ 1 - (\eta(l + \frac{1}{2}))^2 \right]^{1/2} \eta - \frac{1}{3} \leq \frac{5}{4} \eta^{3/2}
\]  

(39)

The proof of (39) uses convexity of \(x(1 - x)^{1/2}\) for \(0 \leq x \leq 1\) and a careful estimate of the error term arising at 0 and 1. (39) yields the following differential inequality for the solution \(\varphi\) of (5)

\[
-\frac{1}{r}(r\varphi)'' + 2q\varphi^{3/2} - \frac{1}{3} r^{-1/2} \varphi^{3/4} \left( 1 - \frac{r\varphi^{1/2}}{4} \right) + \leq -\frac{1}{r}(r\varphi)'' + \sum_{l=0}^{\infty} \frac{q(2l + 1)}{\pi r^2} \left( \varphi(r) - \frac{(l + \frac{1}{2})^2}{r^2} \right)^{1/2} +
\]  

(40)

\[
\leq -\frac{1}{r}(r\varphi)'' + 2q\varphi^{3/2} + \frac{5}{4} r^{-1/2} \varphi^{3/4}
\]

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This allows the second function of the right hand side of (35) as comparison function, which proves (35).

The monotonicity of \( \varphi_Z \) in \( Z \) is immediate by comparison. The convergence of \( \varphi_Z \) to \( \varphi_\infty \) follows also immediately.

To obtain (37) we use the comparison function

\[
\frac{1}{dr} + \frac{2d^{1/2}}{r^{5/2}} + \frac{d^2}{r^4}
\]

with \( c = \left[ \frac{27}{38} + \left( \frac{(27/38)^2 - 2}{9} \right)^{1/2} \right] \) for the bound from above and

\[
\varphi_{TF}(r) - \frac{5}{4} r^{-5/2} \left( d + \frac{r}{2} \right)^{1/2}
\]

as the comparison function from below. By the limiting function for the Thomas-Fermi model (31) the equation (37) follows. Equation (38) follows from (35) and the following observations. Suppose there was a radius \( R \) such that \( \varphi \equiv 0 \) for \( r \) bigger than \( R \). Denote by \( R \) the minimum over all such \( R \). Since

\[
\varphi(R) = 0.
\]

Because of the continuity of \( \varphi \) we can choose a \( \delta \) such that for all \( x \) with \( |x - R| < \delta, \varphi(x)| < 1/8R^2 \) holds. Thus \( \rho_0, \rho_1, \ldots \) is zero also to the left of \( R \), which is a contradiction. Thus there exists a sequence \( r_n \) such that \( r_n \to \infty \) and \( \varphi(r_n) \geq 1/4r_n^2 \). Now use a comparison between \( r_n \) and \( r_{n+1} \) with comparison function \( 1/4r^2 \) to obtain the result.

• The Schrödinger equation

Let \( \rho_Q \) be the ground state density, i.e.,

\[
\rho_Q^Z(r) = N \int dr_1^2 \ldots dr_N^2 \sum_{\sigma_1, \ldots, \sigma_N = 1} |\psi_Z(r, \sigma_1, \sigma_2, \ldots, \sigma_N, N)|^2
\]

where \( \psi_Z \) is the ground state of (8). Let \( \rho_{TF} \) be the Thomas-Fermi density for charge 1, \( \Omega \) a measurable set in \( \mathbb{R}^3 \). Then

\[
\int_{\Omega} Z^{-2} \rho_Q^Z(Z^{-1/3}r) d^3r \to \int_{\Omega} \rho_{TF}(r)d^3r
\]

holds (Lieb and Simon [13]).
References


